07-26-00

Docket No. 004742/AMI-00-07

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Box Patent Application
Assistant Commissioner for Patents
Washington, D.C. 20231

A

Re: Inventor(s): Moris Kori, Alfred W. Mak, Jeong Soo Byun, Lawrence Chung-Lai Lei; and Hua Chung
Title: METHOD AND SYSTEM FOR CONTROLLING THE PRESENCE OF FLUORINE IN REFRACTORY METAL LAYERS

Transmitted herewith is the patent application identified above, including:

X Specification, claims and abstract, totaling 15 pages, excluding Title Sheet.

X Drawings totaling 11 pages, __ Formal _X_ Informal.

__ Declaration and Power of Attorney.

__ Assignment of the invention to **Applied Materials, Inc.**

__ Assignment Recordation Cover Sheet

X Information Disclosure Statement and Form 1449 along with copies of (5) five references recited therein

FEE CALCULATION

Fee Items	Claims Filed	Included With Basic Fee	Extra Claims	Fee Rate	Total
Total Claims 20	20	20-20 = 0	0	X $	--
Independent Claims	4	4 - 3 = 1	1	$78	$78
Basic Filing Fee				$690	$690
TOTAL FEES					$768

XX The Commissioner is hereby authorized to charge $768.00 Deposit Account No. 50-1074.

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XX Please address all future correspondence to:

PATENT COUNSEL
APPLIED MATERIALS, INC.
Legal Affairs Department
P.O.BOX 450A
Santa Clara, CA. 95052

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Signature Robert Mulcahy

Respectfully submitted,

Robert Mulcahy
Registration No. 28,436

PATENT

Atty. Docket No.: 4742/AMI-00-07

PATENT APPLICATION

METHOD AND SYSTEM FOR CONTROLLING THE PRESENCE OF FLUORINE IN REFRACTORY METAL LAYERS

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METHOD AND SYSTEM FOR CONTROLLING THE PRESENCE OF FLUORINE IN REFRACTORY METAL LAYERS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a divisional patent application of United States patent application number 09/605,593 assigned to Applied Materials, Inc. and having Moris Kori, Alfred W. Mak, Jeong Soo Byun, Lawrence Chung-Lai Lei and Hua Chung identified as co-inventors.

BACKGROUND OF THE DISCLOSURE

Field of the Invention

This invention relates to the processing of semiconductor substrates. More particularly, this invention relates to improvements in the process of depositing refractory metal layers on semiconductor substrates.

Description of the Related Art

The semiconductor processing industry continues to strive for larger production yields while increasing the uniformity of layers deposited on substrates having increasing larger surface areas. These same factors in combination with new materials also provide higher integration of circuits per unit area of the substrate. As circuit integration increases, the need for greater uniformity and process control regarding layer thickness rises. As a result, various technologies have been developed to deposit layers on substrates in a cost-effective manner, while maintaining control over the characteristics of the layer. Chemical Vapor Deposition (CVD) is one of the most common deposition processes employed for depositing layers on a substrate. CVD is a flux-dependent deposition technique that requires precise control of the substrate temperature and precursors introduced into the processing chamber in order to produce a desired layer of uniform thickness. These requirements become more critical as substrate size increases, creating a need for more complexity in chamber design and gas flow technique to maintain adequate uniformity.

A variant of CVD that demonstrates superior step coverage, compared to CVD, is Atomic Layer Deposition (ALD). ALD is based upon Atomic Layer Epitaxy (ALE) that was originally employed to fabricate electroluminescent displays. ALD employs

chemisorption to deposit a saturated monolayer of reactive precursor molecules on a substrate surface. This is achieved by alternatingly pulsing an appropriate reactive precursor into a deposition chamber. Each injection of a reactive precursor is separated by an inert gas purge to provide a new atomic layer additive to previous deposited layers to form a uniform layer on the substrate. The cycle is repeated to form the layer to a desired thickness. A drawback with ALD techniques is that the deposition rate is much lower than typical CVD techniques by at least one order of magnitude.

Employing the aforementioned deposition techniques it is seen that formation of a layer at a high deposition rate while providing adequate step coverage are conflicting characteristics often necessitating sacrificing one to obtain the other. This has been prevalent when depositing refractory metal layers to cover gaps or vias during formation of contacts that interconnect adjacent metallic layers separated by a dielectric layer. Historically, CVD techniques have been employed to deposit conductive material in order to inexpensively and quickly form contacts. Due to the increasing integration of semiconductor circuitry, tungsten has been used based upon the superior step coverage of tungsten. As a result, deposition of tungsten employing CVD techniques enjoys wide application in semiconductor processing due to the high throughput of the process.

Depositing tungsten in this manner, however, is attendant with several disadvantages. For example, blanket deposition of a tungsten layer on a semiconductor wafer is time-consuming at temperatures below 400° C. The deposition rate of tungsten may be improved by increasing the deposition temperature to, e.g., about 500° C to about 550° C. Temperatures in this range may compromise the structural and operational integrity of the underlying portions of the integrated circuit being formed. Tungsten has also frustrated photolithography steps during the manufacturing process by providing a relatively rough surface having a reflectivity of 20% or less than that of a silicon substrate. Finally, tungsten has proven difficult to deposit uniformly. This has been shown by variance in tungsten layers' thickness of greater than 1%, which frustrates control of the resistivity of the layer. Several prior attempts to overcome the aforementioned drawbacks have been attempted.

For example, in United States patent number 5,028,565 to Chang et al., which is assigned to the assignee of the present invention, a method is disclosed to improve, inter

alia, uniformity of tungsten layers by varying the deposition chemistry. The method includes, in pertinent part, formation of a nucleation layer over an intermediate barrier layer before depositing the tungsten layer via bulk deposition. The nucleation layer is formed from a gaseous mixture of tungsten hexafluoride, hydrogen, silane and argon. The nucleation layer is described as providing a layer of growth sites to promote uniform deposition of a tungsten layer. The benefits provided by the nucleation layer are described as being dependent upon the barrier layer present. For example, were the barrier layer formed from titanium nitride the tungsten layer's thickness uniformity is improved as much as 15%. Were the barrier layer formed from sputtered tungsten or sputtered titanium tungsten the benefits provided by the nucleation layer are not substantial.

A need exists, therefore, to provide techniques to improve the characteristics of refractory metal layers deposited on semiconductor substrates.

SUMMARY OF THE INVENTION

A method and system reduces the resistance of contacts of refractory metal layers by controlling the presence of fluorine contained therein. The present invention is based upon the discovery that when employing ALD techniques to form refractory metal layers on a substrate, the carrier gas employed impacts the presence of fluorine in the resulting layer. As a result, the method features chemisorbing onto the substrate alternating monolayers of a first compound and a second compound, with the second compound having fluorine atoms associated therewith, with each of the first and second compounds being introduced into the processing chamber along with a carrier gas; and controlling a quantity of the fluorine atoms associated with the monolayer of the second compound as a function of the carrier gas. Specifically, it was found that by introducing the first and second compounds employing H_2 as a carrier gas, the amount of fluorine present in the resulting refractory metal layer was substantially reduced, compared to employing either nitrogen, N_2, or argon, Ar, as a carrier gas.

To that end, the system includes a processing chamber, having a holder, disposed therein to support the substrate. A gas delivery system and a pressure control system are in fluid communication with the processing chamber. A temperature control system is in thermal communication therewith. A controller is in electrical

communication with gas delivery system, temperature control system, and the pressure control system. A memory is in data communication with the controller. The memory comprises a computer-readable medium having a computer-readable program embodied therein. The computer-readable program includes instructions for controlling the operation of the processing chamber.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a perspective view of a semiconductor processing system in accordance with the present invention;

Fig. 2 is a detailed view of the processing chambers shown above in Fig. 1;

Fig. 3 is a schematic view showing deposition of a first molecule onto a substrate during ALD;

Fig. 4 is a schematic view showing deposition of second molecule onto a substrate during ALD to form a refractory metal layer;

Fig. 5 is a graphical representation showing the concentration of gases, introduced into the processing chamber shown above in Fig. 2, and the time in which the gases are present in the processing chamber, in accordance with the present invention;

Fig. 6 is a graphical representation showing the relationship between the number of ALD cycles and the thickness of a layer formed on a substrate employing ALD, in accordance with the present invention;

Fig. 7 is a graphical representation showing the relationship between the number of ALD cycles and the resistivity of a layer formed on a substrate employing ALD, in accordance with the present invention;

Fig. 8 is a graphical representation showing the relationship between the deposition rate of a layer formed on a substrate employing ALD and the temperature of the substrate;

Fig. 9 is a graphical representation showing the relationship between the resistivity of a layer formed on a substrate employing ALD and the temperature of the substrate, in accordance with the present invention;

Fig. 10 is a cross-sectional view of a patterned substrate having a nucleation layer formed thereon employing ALD, in accordance with the present invention;

Fig. 11 is a partial cross-sectional view of the substrate, shown above in Fig. 10, with a refractory metal layer formed atop of the nucleation layer employing CVD, in accordance with the present invention;

Fig. 12 is a graphical representation showing the concentration of gases shown above in Fig. 5 in accordance with a first alternate embodiment of the present invention;

Fig. 13 is a graphical representation showing the concentration of gases shown above in Fig. 5 in accordance with a second alternate embodiment of the present invention;

Fig. 14 is a graphical representation showing the fluorine content versus depth of a refractory metal layer formed on a substrate employing ALD either Ar or N_2 being a carrier gas; and

Fig. 15 is a graphical representation showing the fluorine content versus depth of a refractory metal layer formed on a substrate employing ALD with H_2 being a carrier gas.

DETAILED DESCRIPTION OF THE INVENTION

Referring to Fig. 1, an exemplary wafer processing system includes two or more processing chambers 12 and 14 disposed in a common work area 16 surrounded by a wall 18. The processing chambers 12 and 14 are in data communication with a controller 22 that is connected to one or more monitors, shown as 24 and 26. The monitors typically display common information concerning the process associated with the processing chambers 12 and 14. One of the monitors 26 is mounted to the wall 18, with the remaining monitor 24 being disposed in the work area 16. Operational control of the processing chambers 12 and 14 may be achieved use of a light pen, associated with one of the monitors 24 and 26, to communicate with the controller 22. For example, light pen 28

is associated with monitor 24 and facilitates communication with the controller 22 through monitor 24. Light pen 30 facilitates communication with the controller 22 through monitor 26.

Referring both the to Figs. 1 and 2, each of the processing chambers 12 and 14 includes a housing 30 having a base wall 32, a cover 34, disposed opposite to the base wall 32, and a sidewall 36, extending therebetween. The housing 30 defines a chamber 37, and a pedestal 38 is disposed within the processing chamber 37 to support a substrate 42, such as a semiconductor wafer. The pedestal 38 may be mounted to move between the cover 34 and the base wall 32, using a displacement mechanism (not shown). Supplies of processing gases 39a, 39b and 39c are in fluid communication with the processing chamber 37 via a showerhead 40. Regulation of the flow of gases from the supplies 39a, 39b and 39c is effectuated via flow valves 41.

Depending on the specific process, the substrate 42 may be heated to a desired temperature prior to layer deposition via a heater embedded within the pedestal 38. For example, the pedestal 38 may be resistively heated by applying an electric current from an AC power supply 43 to the heater element 44. The wafer 40 is, in turn, heated by the pedestal 38, and can be maintained within a desired process temperature range of, for example, about 20 °C to about 750 °C. A temperature sensor 46, such as a thermocouple, is also embedded in the wafer support pedestal 38 to monitor the temperature of the pedestal 38 in a conventional manner. For example, the measured temperature may used in a feedback loop to control the electrical current applied to the heater element 44 by the power supply 43, such that the wafer temperature can be maintained or controlled at a desired temperature which is suitable for the particular process application. The pedestal 38 is optionally heated using radiant heat (not shown). A vacuum pump 48 is used to evacuate the processing chamber 37 and to help maintain the proper gas flows and pressure inside the processing chamber 37.

Referring to Figs. 1 and 3, one or both of the processing chambers 12 and 14, discussed above may operate to deposit refractory metal layers on the substrate employing ALD techniques. Depending on the specific stage of processing, the refractory metal layer may be deposited on the material from which the substrate 42 is fabricated, e.g., SiO_2. The refractory metal layer may also be deposited on a layer previously formed on the substrate 42, e.g., titanium, titanium nitride and the like.

ALD proceeds by chemisorption. The initial surface of the substrate 42 presents an active ligand to the process region. A batch of a first processing gas, in this case Aa_x, results in a layer of A being deposited on the substrate 42 having a surface of ligand x exposed to the processing chamber 37. Thereafter, a purge gas enters the processing chamber 37 to purge the gas Aa_x. After purging gas Aa_x from the processing chamber 37, a second batch of processing gas, Bb_y, is introduced into the processing chamber 37. The a ligand present on the substrate surface reacts with the b ligand and B atom on the, releasing molecules ab and Ba, that move away from the substrate 42 and are subsequently pumped from the processing chamber 37. In this manner, a surface comprising a monolayer of A atoms remains upon the substrate 42 and exposed to the processing chamber 37, shown in Fig. 4. The process proceeds cycle after cycle, until the desired thickness is achieved.

Referring to both Figs. 2 and 5, although any type of processing gas may be employed, in the present example, the processing gas Aa_x is WF_6 and the processing gas Bb_y is B_2H_6. Two purge gases were employed: Ar and N_2. Each of the processing gases is flowed into the processing chamber 37 with a carrier gas, which in this example were one of the purge gases: WF_6 is introduced with Ar and B_2H_6 is introduced with N_2. It should be understood, however, that the purge gas may differ from the carrier gas, discussed more fully below. One cycle of the ALD technique in accordance with the present invention includes flowing the purge gas, N_2, into the processing chamber 37 during time t_1, which is approximately five seconds before B_2H_6 is flowed into the processing chamber 37. During time t_2, the processing gas B_2H_6 is flowed into the processing chamber 37 for approximately five seconds, along with a carrier gas, which in this example is N_2. After five seconds have lapsed, the flow of B_2H_6 terminates and the flow of N_2 continues during time t_3 for an additional five seconds, purging the processing chamber of B_2H_6. During time t_4, the processing chamber 37 is pumped so as to remove all gases. The pumping process lasts approximately thirty seconds. After pumping of the process chamber 37, the carrier gas Ar is introduced for approximately five seconds during time t_5, after which time the process gas WF_6 is introduced into the processing chamber 37 for about five seconds, along with the carrier gas Ar during time t_6. The flow of the processing gas WF_6 into the processing chamber 37 is terminated approximately five seconds after it commenced. After the flow of WF_6 into the processing chamber 37 terminates, the flow of Ar continues for five additional seconds, during time t_7.

Thereafter, the processing chamber 37 is pumped so as to remove all gases therein, during time t_8. As before, the pumping process lasts approximately thirty seconds, thereby concluding one cycle of the ALD technique in accordance with the present invention.

The benefits of employing ALD are manifold, including flux-independence of layer formation that provides uniformity of deposition independent of the size of a substrate. For example, the measured difference of the layer uniformity and thickness measured between of 200 mm substrate and a 32 mm substrate deposited in the same chamber is negligible. This is due to the self-limiting characteristics of chemisorption. Further, the chemisorption characteristics contribute to near-perfect step coverage over complex topography.

In addition, the thickness of the layer A, shown in Fig. 4, may be easily controlled while minimizing the resistance of the same by employing ALD. With reference to Fig. 6 it is seen the slope of line 50 that the thickness of the tungsten layer A is proportional to the number of cycles employed to form the same. The resistivity of the tungsten layer, however, is relatively independent of the thickness of the layer, as shown by the slope of line 52 in Fig. 7. Thus, employing ALD, the thickness of a refractory metal layer may be easily controlled as a function of the cycling of the process gases introduced into the processing chamber with a negligible effect on the resistivity.

Referring to Fig. 8, control of the deposition rate was found to be dependent upon the temperature of the substrate 42. As shown by the slope of line 54, increasing the temperature of the substrate 42 increased the deposition rate of the tungsten layer A. For example, at 56, the deposition rate is shown to be approximately 2 Å/cycle at 250° C. However at point 58 the deposition rate is approximately 5 Å/cycle at a temperate of 450° C. The resistivity of the tungsten layer, however, is virtually independent of the layer thickness, as shown by the slope of curve 59, shown in Fig. 9. As a result, the deposition rate of the tungsten layer may be controlled as a function of temperature without comprising the resistivity of the same. However, it is preferred to perform many processing steps at temperatures well below 450° C.

To that end, a bifurcated deposition process may be practiced in which nucleation of the refractory metal layer occurs in a different chamber than the formation of the remaining portion of the refractory metal layer. Specifically, in the present example, nucleation of a tungsten layer occurs in chamber 12 employing the ALD techniques discussed above, with the substrate 42 being heated in the range of 200° C to 400° C, and

the processing chamber 37 being pressurized in the range of 1 to 10 Torr. A nucleation layer 60 of approximately 12 to 20 nm is formed on a patterned substrate 42, shown in Fig. 10. As shown, the substrate 42 includes a barrier layer 61 and a patterned layer having a plurality of vias 63. The nucleation layer is formed adjacent to the patterned layer covering the vias 63. As shown, forming the nucleation layer 60 employing ALD techniques provides 100% step coverage. To decrease the time required to form a complete layer of tungsten, a bulk deposition of tungsten onto the nucleation layer 60 occurs using CVD techniques, while the substrate 42 is disposed in processing chamber 14, shown in Fig. 1. The bulk deposition may be performed using recipes well known in the art. In this manner, a tungsten layer 65 providing a complete plug fill is achieved on the patterned layer with vias having aspect ratios of approximately 6:1, shown in Fig. 11.

As mentioned above, in an alternate embodiment of the present invention, the carrier gas may differ from the purge gas, as shown in Fig. 12. The purge gas, which is introduced at time intervals t_1, t_3, t_5 and t_7 comprises of Ar. The carrier gas, which is introduced at time intervals t_2 and t_6, comprises of N_2. Thus, at time interval t_2 the gases introduced into the processing chamber include a mixture of B_2H_6 and N_2, and a time interval t_6, the gas mixture includes WF_6 and N_2. The pump process during time intervals t_4 and t_8 is identical to the pump process discussed above with respect to Fig. 5. In yet another embodiment, shown in Fig. 13, the carrier gas during time intervals t_2 and t_6 comprises H_2, with the purge gas introduced at time intervals t_1, t_3, t_5 and t_7 comprising of Ar. The pump processes at time intervals t_4 and t_8 are as discussed above. As a result, at time interval t_2 the gas mixture introduced into the processing chamber 37 consists of B_2H_6 and H_2, and WF_6 and H_2, at time interval t6.

An advantage realized by employing the H_2 carrier gas is that the stability of the tungsten layer A may be improved. Specifically, by comparing curve 66 in Fig. 14 with the curve 68 in Fig. 15, it is seen that the concentration of fluorine in the nucleation layer 60 is much less when H_2 is employed as the carrier gas, as compared with use of N_2 or Ar as a carrier gas. Specifically, the apex and nadir of curve 66 show that the fluorine concentration reaches levels in excess of $1x10^{21}$ atoms per cubic centimeter and only as low as just below $1x10^{19}$ atoms per cubic centimeter. Curve 68, however, shows that the fluorine concentration is well below $1x10^{21}$ atoms per cubic centimeter at the apex and well below $1x10^{17}$ atoms per cubic centimeter at the nadir. Thus, employing H_2 as the carrier gas provides a much more stable film, i.e., the probability of fluorine diffusing into

the substrate, or adjacent layer is reduced. This also reduces the resistance of the refractory metal layer by avoiding the formation of a metal fluoride that may result from the increased fluorine concentration. Thus, the stability of the nucleation layer, as well as the resistivity of the same, may be controlled as a function of the carrier gas employed. This is also true when a refractory metal layer is deposited entirely employing ALD techniques, i.e., without using other deposition techniques, such as CVD.

Referring again to Fig. 2, the process for depositing the tungsten layer may be controlled using a computer program product that is executed by the controller 22. To that end, the controller 22 includes a central processing unit (CPU) 70, a volatile memory, such as a random access memory (RAM) 72 and permanent storage media, such as a floppy disk drive for use with a floppy diskette, or hard disk drive 74. The computer program code can be written in any conventional computer readable programming language; for example, 68000 assembly language, C, C++, Pascal, Fortran and the like. Suitable program code is entered into a single file, or multiple files, using a conventional text editor and stored or embodied in a computer-readable medium, such as the hard disk drive 74. If the entered code text is in a high level language, the code is compiled and the resultant compiler code is then linked with an object code of precompiled Windows® library routines. To execute the linked and, compiled object code the system user invokes the object code, causing the CPU 70 to load the code in RAM 72. The CPU 70 then reads and executes the code to perform the tasks identified in the program.

Although the invention has been described in terms of specific embodiments, one skilled in the art will recognize that various changes to the reaction conditions, i.e., temperature, pressure, film thickness and the like can be substituted and are meant to be included herein. In addition, other refractory metals may be deposited, in addition to tungsten, and other deposition techniques may be employed in lieu of CVD. For example, physical vapor deposition (PVD) techniques, or a combination of both CVD and PVD techniques may be employed. Therefore, the scope of the invention should not be based upon the foregoing description. Rather, the scope of the invention should be determined based upon the claims recited herein, including the full scope of equivalents thereof.

WHAT IS CLAIMED IS

1. A method for forming a layer on a substrate disposed in a processing chamber, said method comprising:

chemisorbing onto said substrate alternating monolayers of a first compound and a second compound, with said second compound having fluorine atoms associated therewith, with each of said first and second compounds being introduced into said processing chamber along with a carrier gas; and

controlling a quantity of said fluorine atoms associated with the monolayer of said second compound as a function of said carrier gas.

2. The method of claim 1 wherein controlling said quantity of said fluorine atoms further including selecting said carrier gas from a group of gases consisting of nitrogen (N_2), argon (Ar), hydrogen (H_2).

3. The method as recited in claim 1 wherein said first compound includes a boron-containing compound.

4. The method of claim 1 wherein said refractory metal is selected from the group consisting of titanium (Ti) and tungsten (W).

5. The method of claim 1 further including purging said processing chamber following chemisorption of each of the alternating monolayers.

6. The method as recited in claim 3 wherein purging said processing chamber includes introducing a purge gas therein.

7. The method as recited in claim 3 wherein purging said processing chamber includes pumping said processing chamber to evacuate all gases disposed therein.

8. The method as recited in claim 3 wherein purging of said processing chamber includes introducing a purge gas therein and subsequently pumping said processing chamber clear of all gases disposed therein.

9. The method as recited in claim 6 wherein said purge gas and said carrier gas have identical constituents selected from a group consisting of nitrogen (N_2), argon (Ar), hydrogen (H_2).

10. A method for forming a layer on a substrate, said method comprising:

serially exposing said substrate to first and second reactive gases, with said first reactive gas having a first compound associated therewith and said second reactive gas having a second compound associated therewith, to form alternating monolayers of said first compound and said second compound, with said second compound having fluorine atoms associated therewith;

controlling a quantity of said fluorine atoms associated with the monolayer of said second compound by introducing into said processing chamber a carrier gas along with said first and second reactive gases; and

purging said processing chamber following chemisorption of each of the alternating monolayers.

11. The method as recited in claim 10 wherein purging said processing chamber includes introducing a purge gas therein.

12. The method as recited in claim 11 wherein purging said processing chamber includes pumping said processing chamber to evacuate all gases disposed therein.

13. The method as recited in claim 12 wherein said first compound includes a diborane (B_2H_6) said second compound is tungsten (W).

14. The method as recited in claim 13 wherein said purge gas and said carrier gas have identical constituents selected from a group consisting of nitrogen (N_2), argon (Ar), hydrogen (H_2).

15. A processing system for processing a substrate in a processing chamber, said system comprising:

means for chemisorbing, onto said substrate, alternating monolayers of a first compound and a second compound, with said second compound having fluorine atoms associated therewith, with each of said first and second compounds being introduced into said processing chamber along with a carrier gas; and

means for controlling a quantity of said fluorine atoms associated with the monolayer of said second compound as a function of said carrier gas.

16. A processing system for a substrate, said system comprising:

a body defining a processing chamber;

a holder disposed within said processing chamber to support said substrate;

a gas delivery system in fluid communication with said processing chamber;

a first temperature control system in thermal communication with said processing chamber;

a pressure control system in fluid communication with said processing chamber;

a controller in electrical communication with said gas delivery system, said temperature control system, and said pressure control system; and

a memory in data communication with said controller, said memory comprising a computer-readable medium having a computer-readable program embodied therein, said computer-readable program including a first set of instructions for controlling said gas delivery system to chemisorb, onto said substrate, alternating monolayers of a first compound and a second compound, with said second compound having fluorine atoms associated therewith, with each of said first and second compounds being introduced into said processing chamber along with a carrier gas; and a second set of instructions to control said gas delivery system to control a quantity of said fluorine atoms associated with the monolayer of said second compound controlling a quantity of said fluorine atoms associated with the monolayer of said second compound by introducing, into said processing chamber, a carrier gas along with said first and second reactive gases.

17. The processing system as recited in claim 16 wherein said computer-readable program includes an additional set of instructions to control said gas system to purge said processing chamber by introducing a purge gas therein following chemisorption of each of the alternating monolayers.

18. The processing system as recited in claim 16 wherein said computer-readable program includes a further set of instructions to control said pressure control system to purge said processing chamber by evacuating said processing chamber following chemisorption of each of the alternating monolayers.

19. The processing system as recited in claim 16 wherein said compound includes a boron-containing compound and said second compound includes a refractory metal compound with said refractory metal compound being from the group consisting of titanium and tungsten and said purge gas and carrier gases each being from the group consisting of nitrogen (N_2), hydrogen (H_2) and argon (Ar).

20. The processing system as recited in claim 19 wherein said purge gas and said carrier gas having differing constituents.

METHOD AND SYSTEM FOR CONTROLLING THE PRESENCE OF FLUORINE IN REFRACTORY METAL LAYERS

ABSTRACT OF THE DISCLOSURE

A method and system to reduce the resistance of refractory metal layers by controlling the presence of fluorine contained therein. The present invention is based upon the discovery that when employing ALD techniques to form refractory metal layers on a substrate, the carrier gas employed impacts the presence of fluorine in the resulting layer. As a result, the method features chemisorbing, onto the substrate, alternating monolayers of a first compound and a second compound, with the second compound having fluorine atoms associated therewith, with each of the first and second compounds being introduced into the processing chamber along with a carrier gas to control a quantity of the fluorine atoms associated with the monolayer of the second compound.

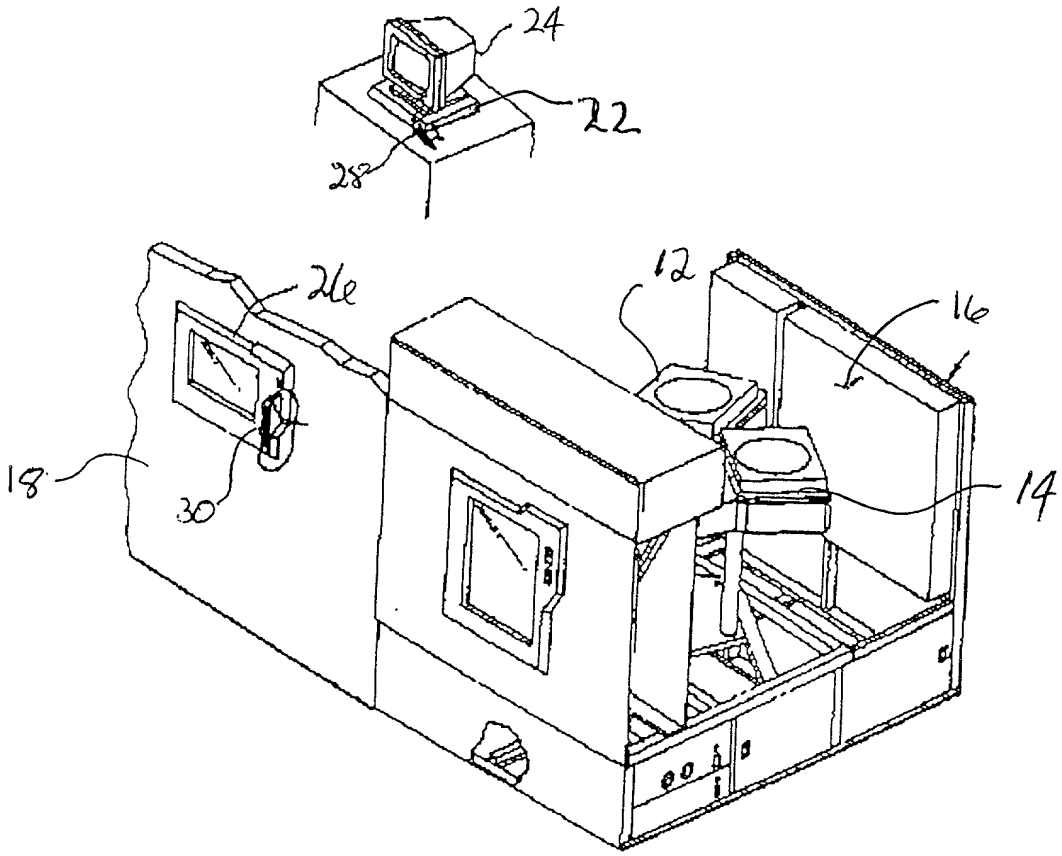
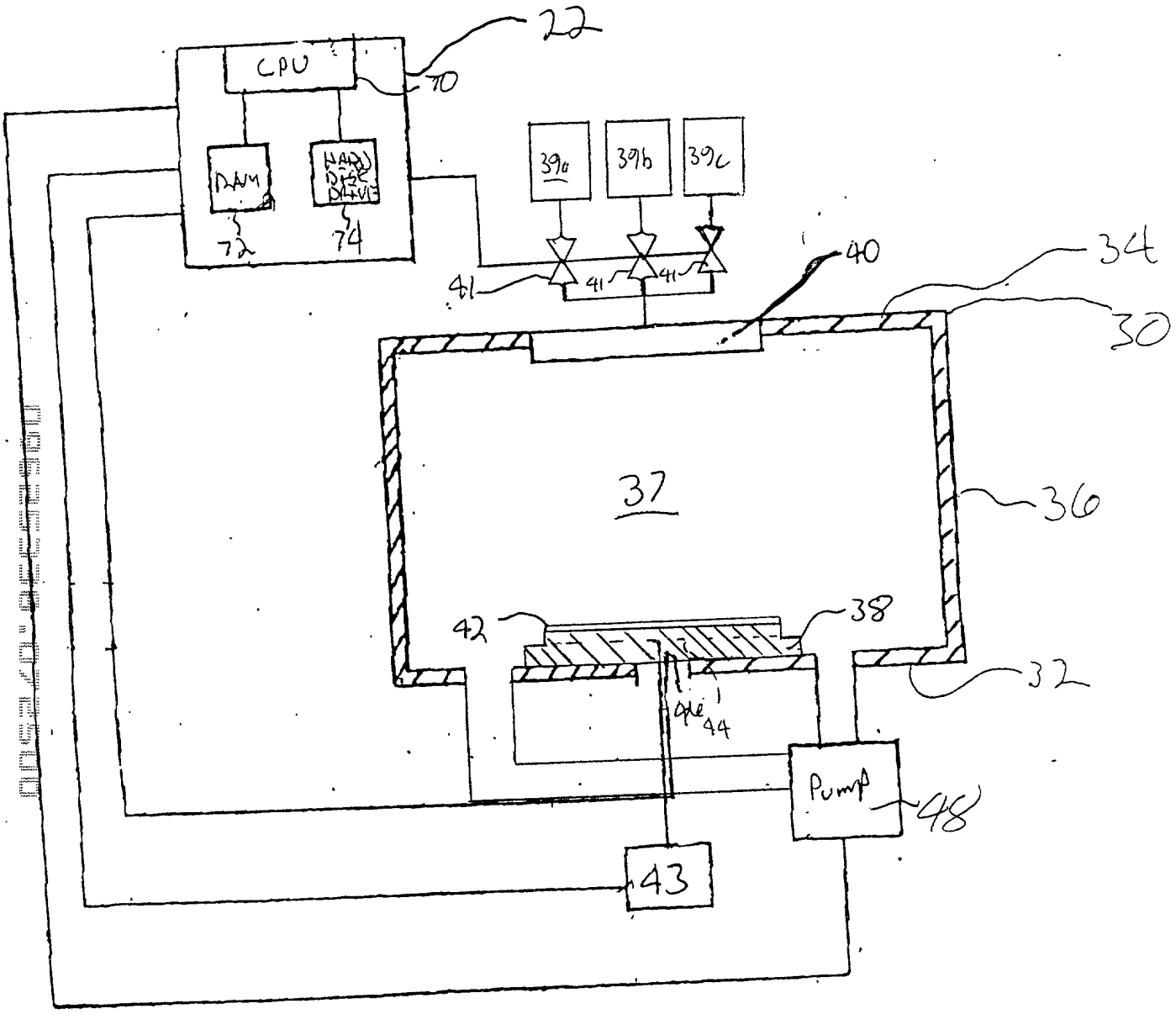


Fig. 1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CPU
70
RAM
72
HARD DISK DRIVE
74
39a
39b
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37
36
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38
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Pump
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Fig. 2

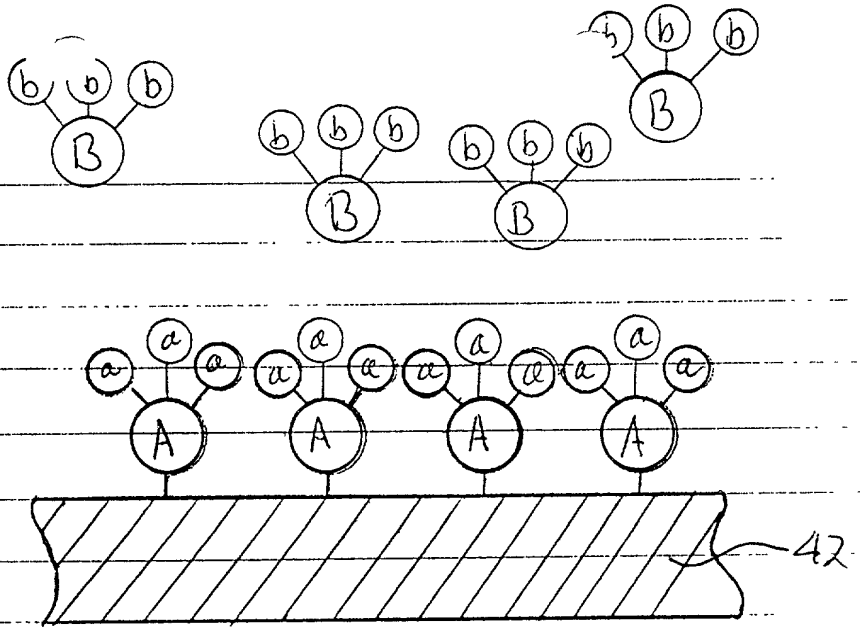


FIG. 3

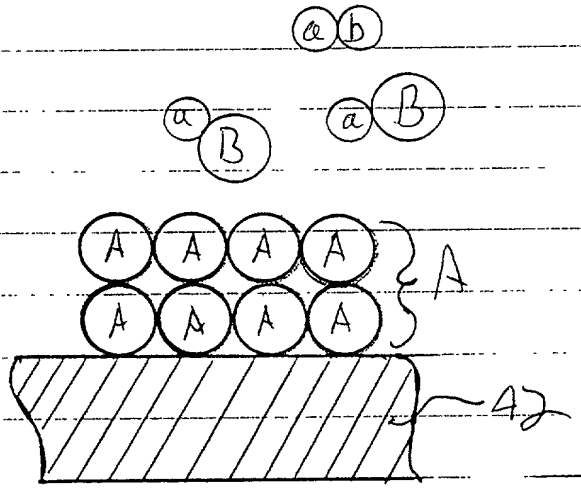


FIG. 4

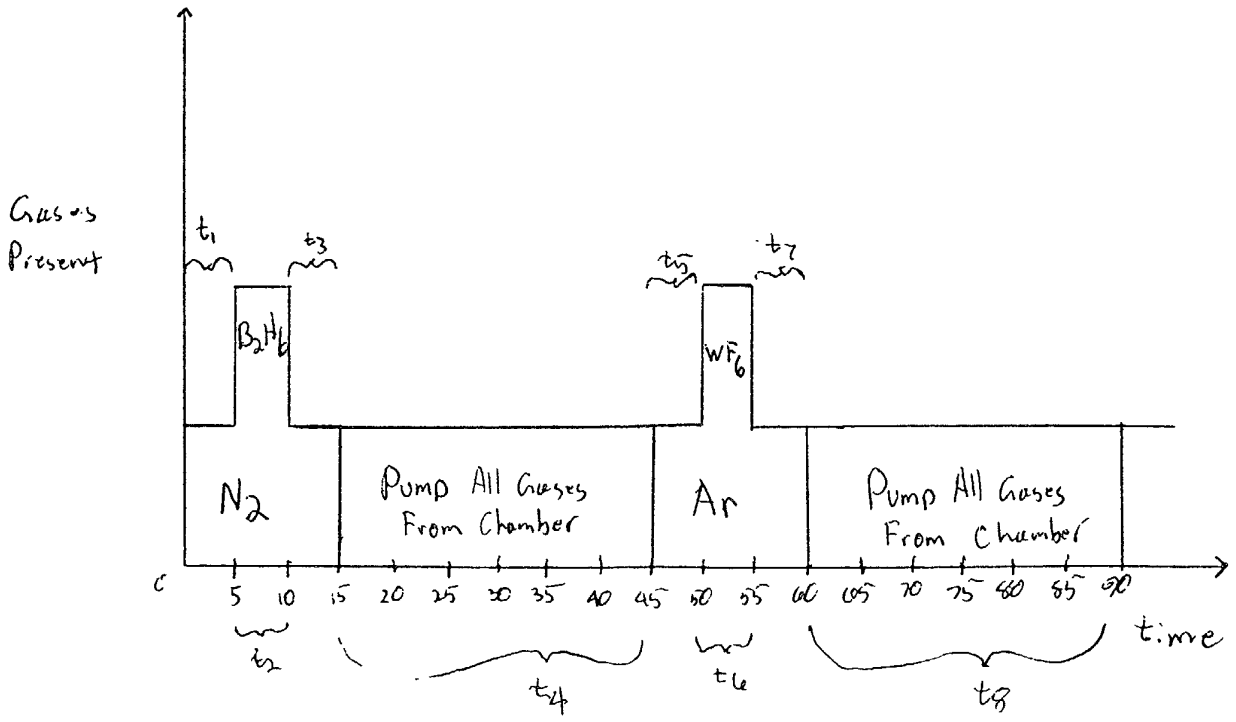

Gases Present
t_1
t_3
t_5
t_7
B_2H_6
WF_6
N_2
Pump All Gases From Chamber
Ar
Pump All Gases From Chamber
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
time
t_2
t_4
t_6
t_8

Fig. 5

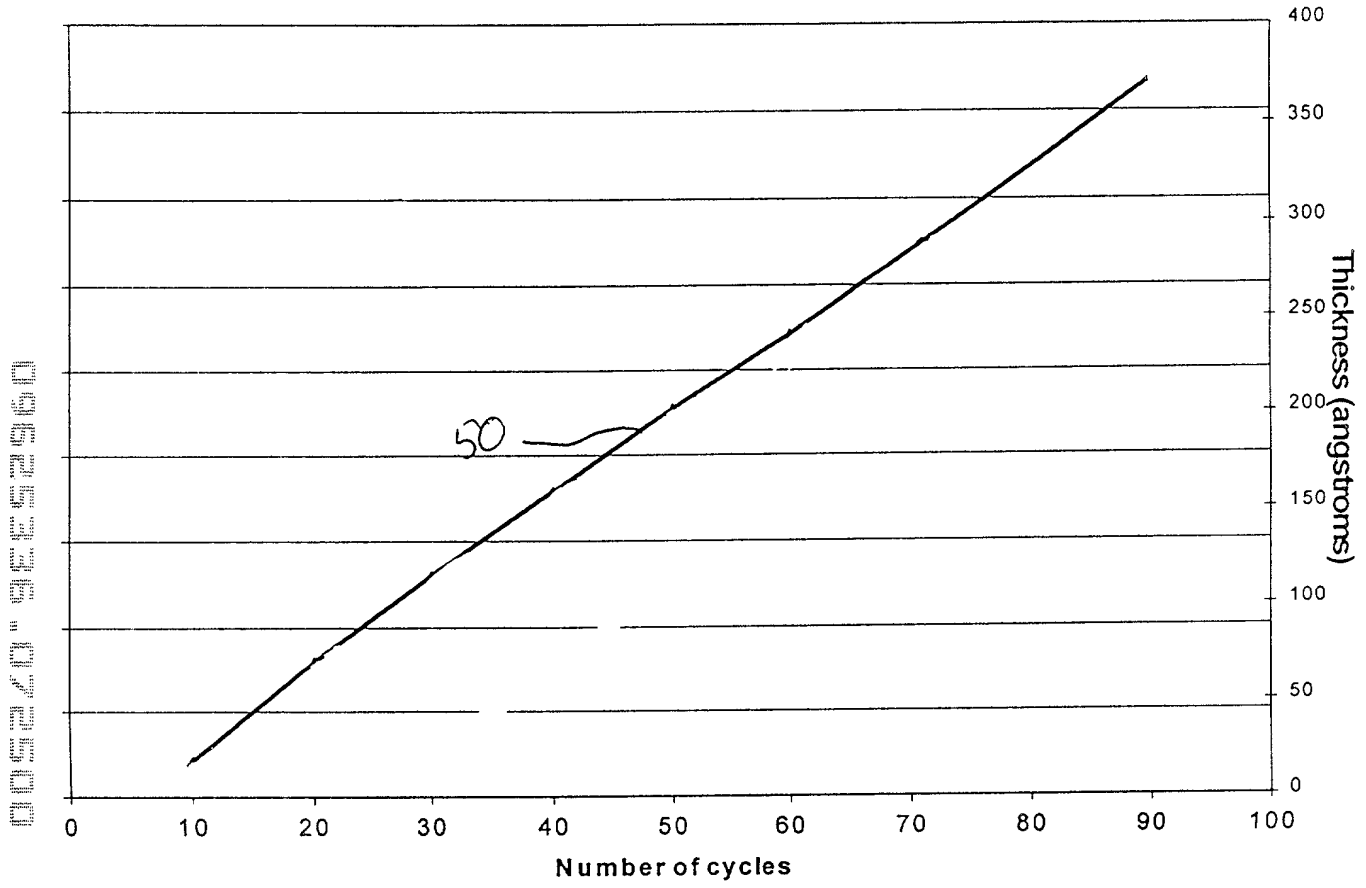

400
350
300
250
200
150
100
50
0
Thickness (angstroms)
0
10
20
30
40
50
60
70
80
90
100
Number of cycles
50

Fig. 6

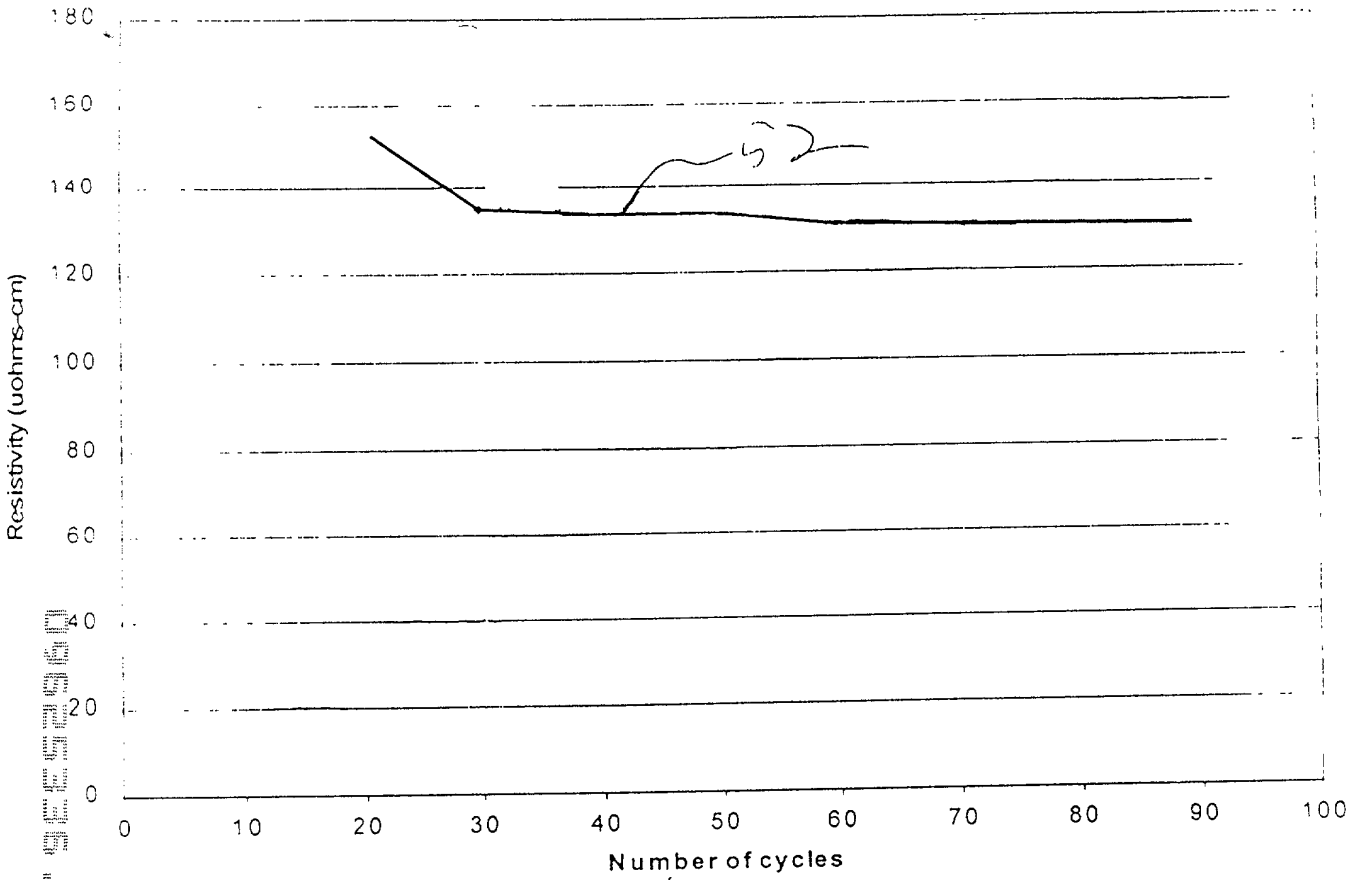

Resistivity (uohms-cm)
180
160
140
120
100
80
60
40
20
0
0
10
20
30
40
50
60
70
80
90
100
Number of cycles
52

FIG. 7

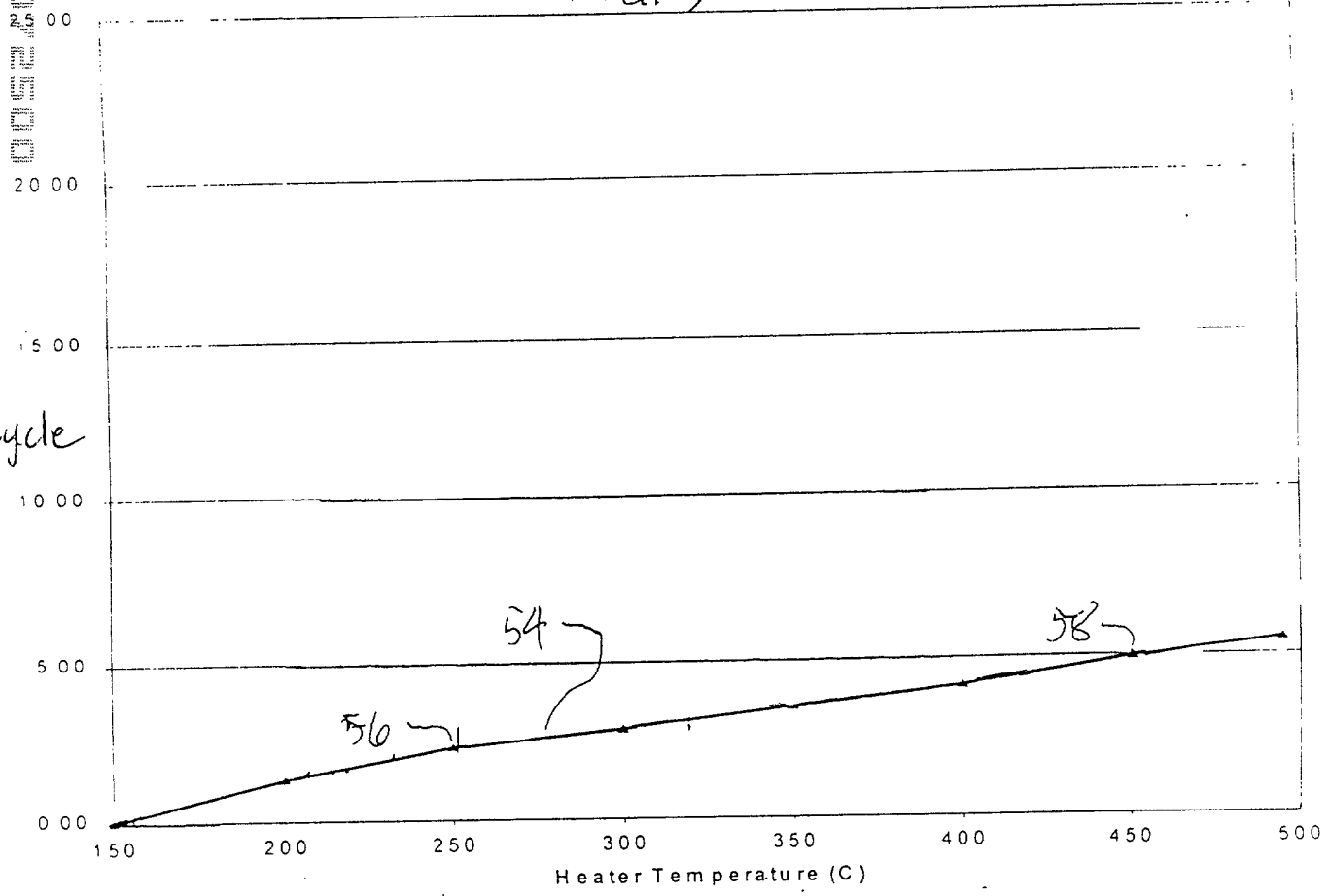

25 00
20 00
15 00
10 00
5 00
0 00
Å/cycle
150
200
250
300
350
400
450
500
Heater Temperature (C)
54
56
58

FIG. 8

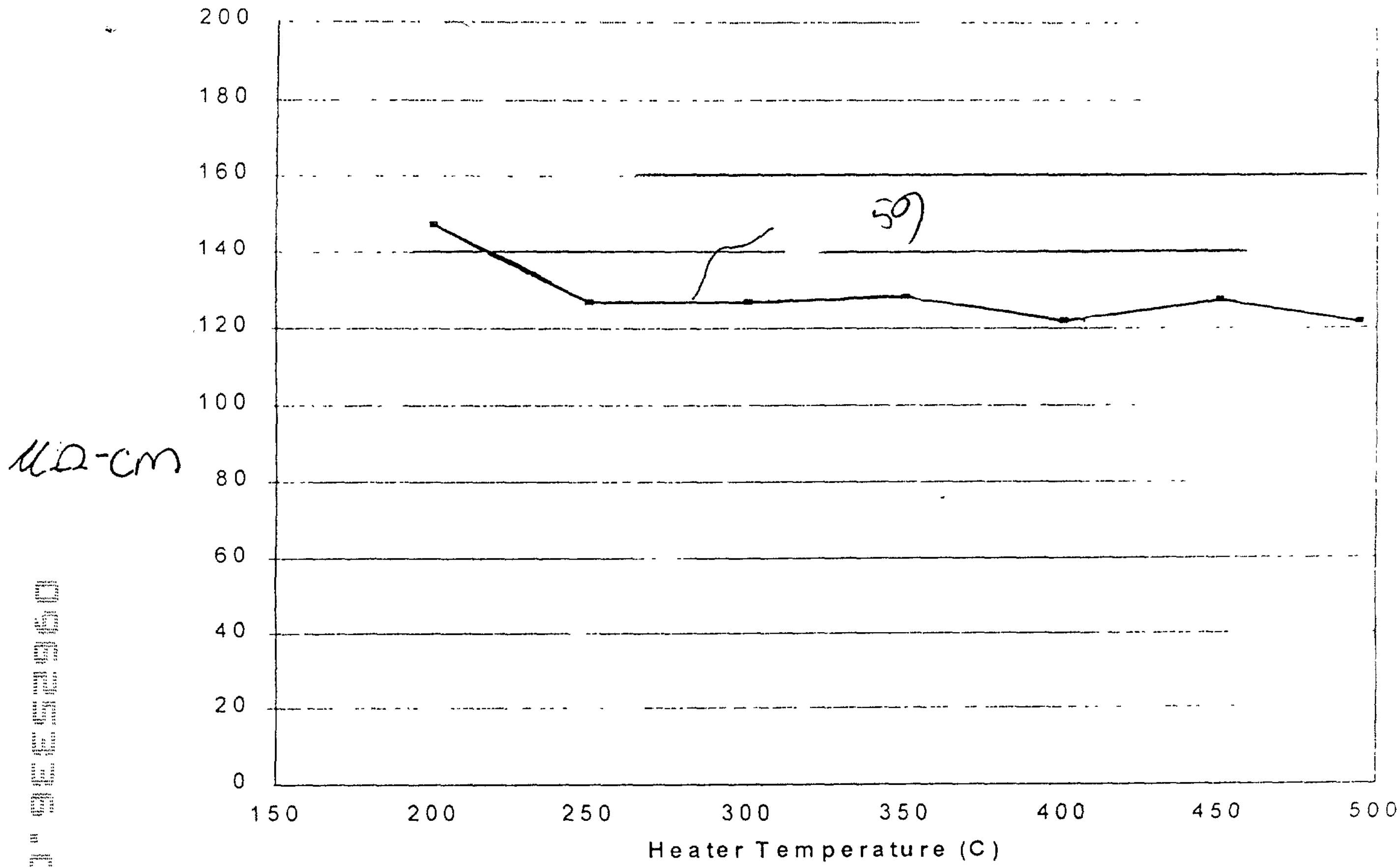


Fig. 9

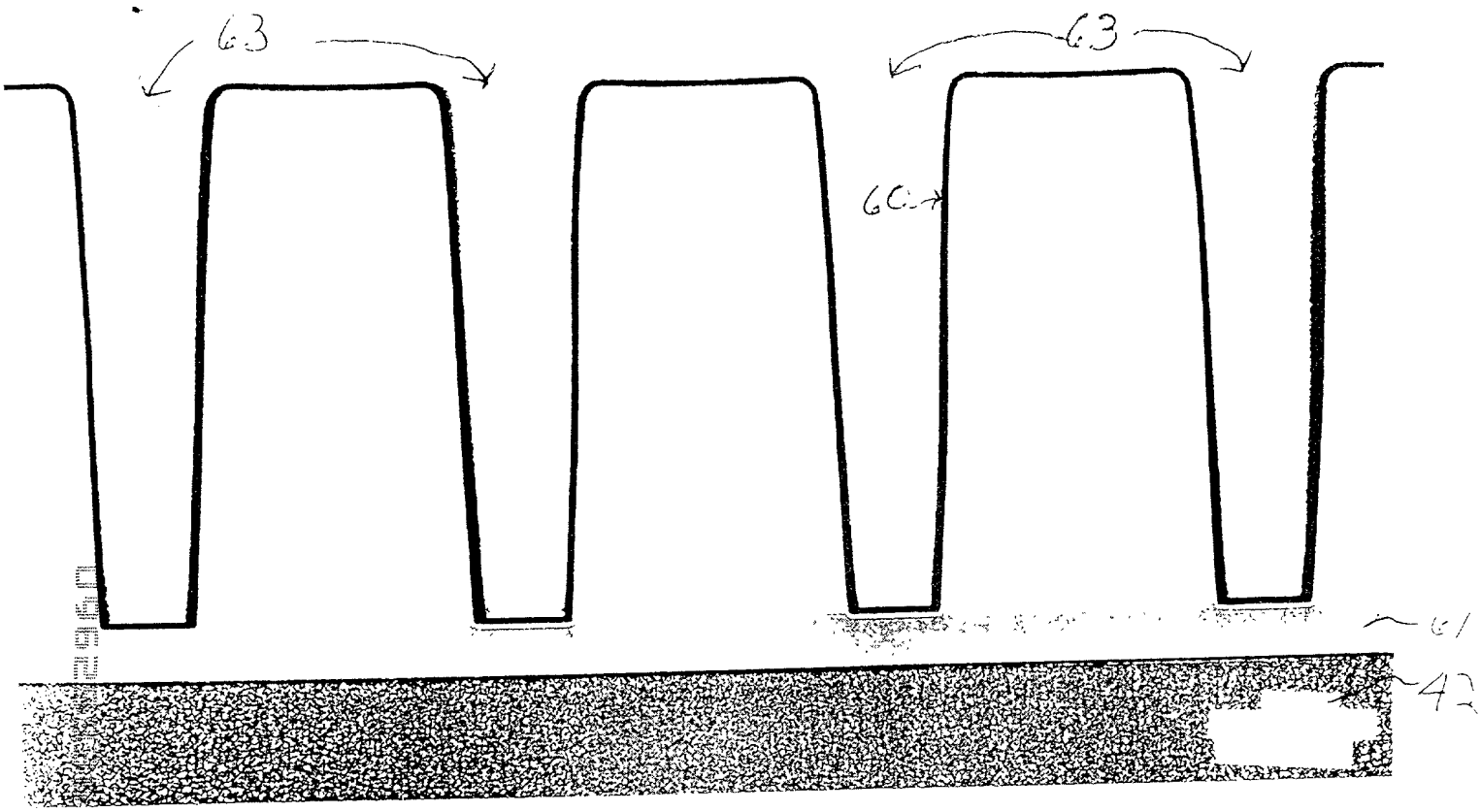


Fig. 10

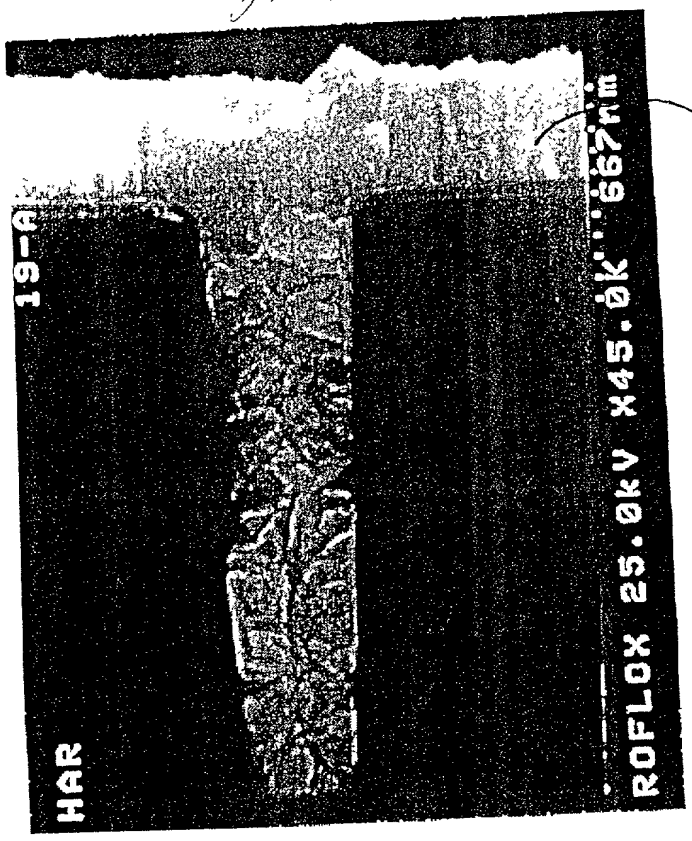


Fig. 11

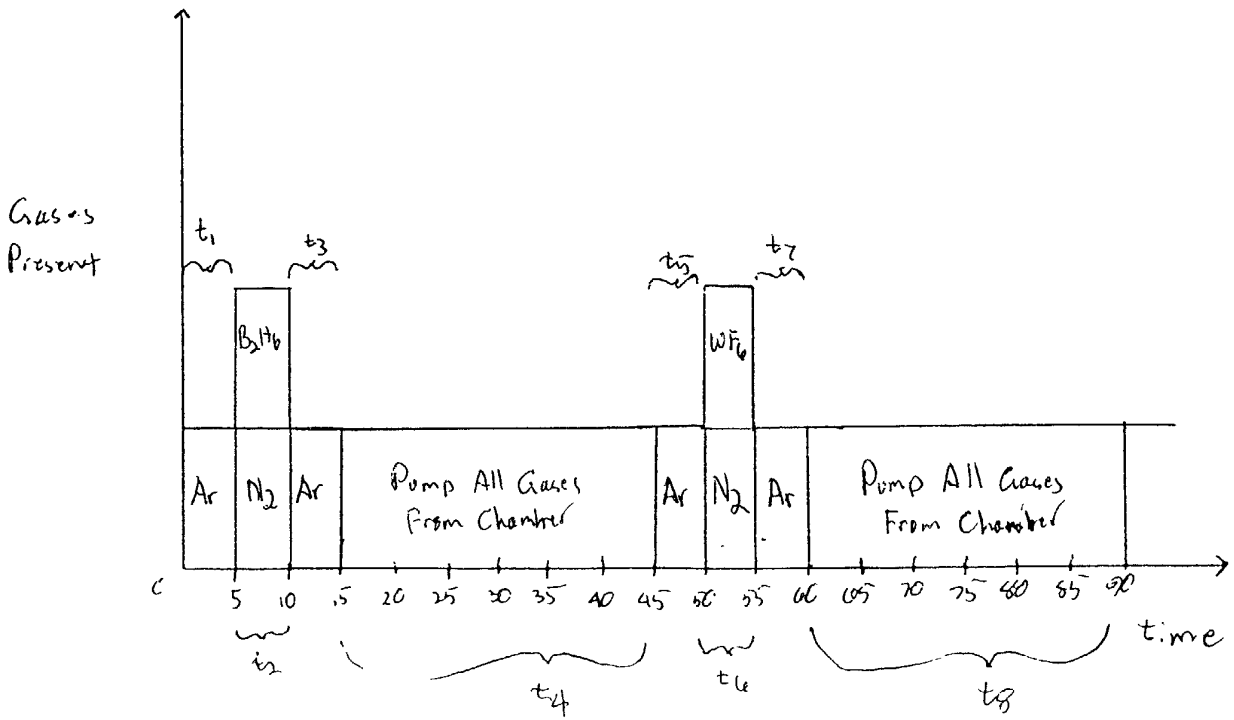
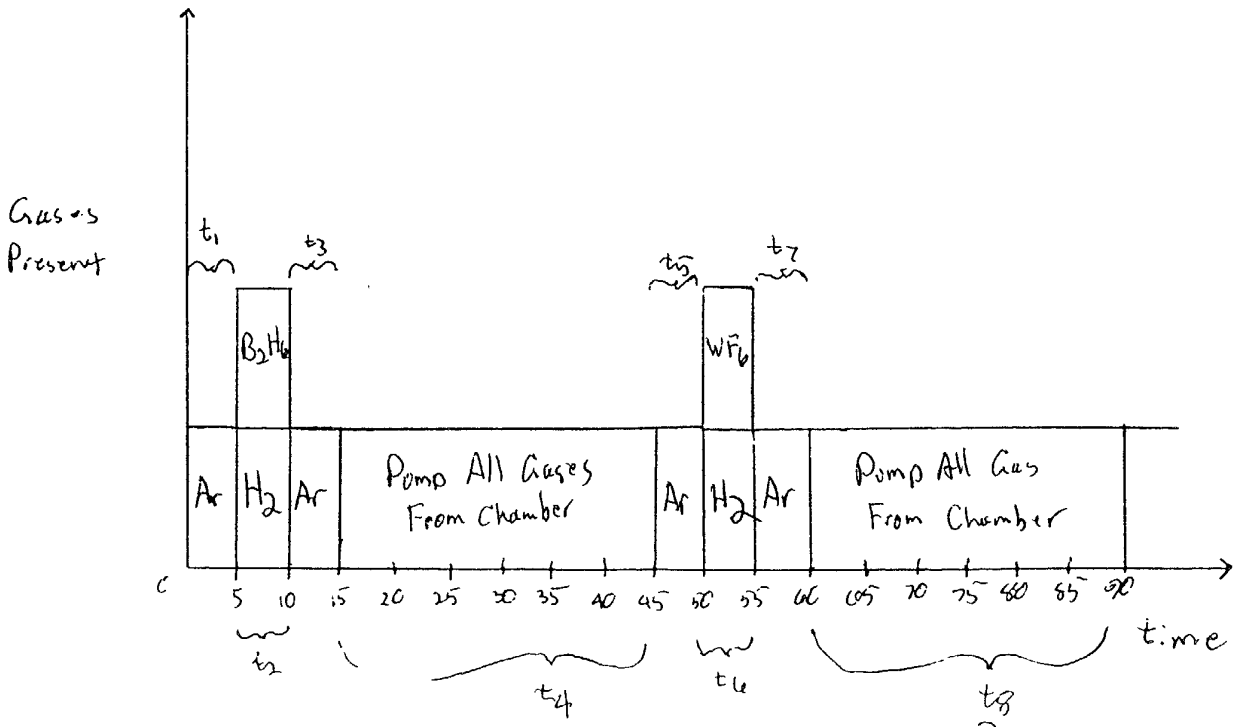

Gases Present
t1
t3
t5
t7
B2H6
WF6
Ar
N2
Ar
Pump All Gases From Chamber
Ar
N2
Ar
Pump All Gases From Chamber
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
time
t2
t4
t6
t8

Fig. 12



Fig, 13

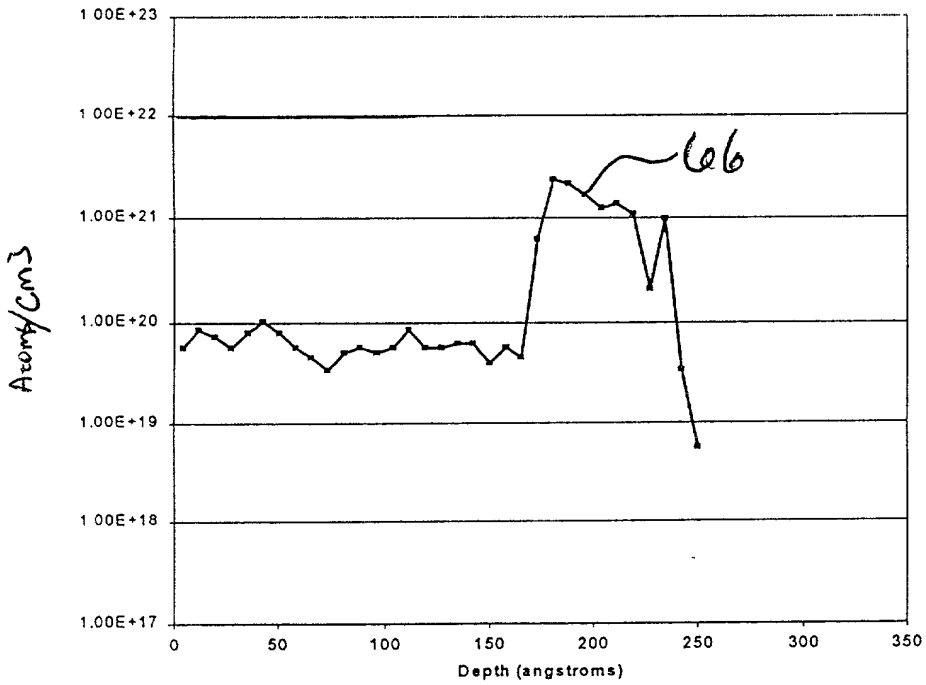

1.00E+23
1.00E+22
1.00E+21
1.00E+20
1.00E+19
1.00E+18
1.00E+17
Atoms/cm3
66
0
50
100
150
200
250
300
350
Depth (angstroms)

Fig. 14

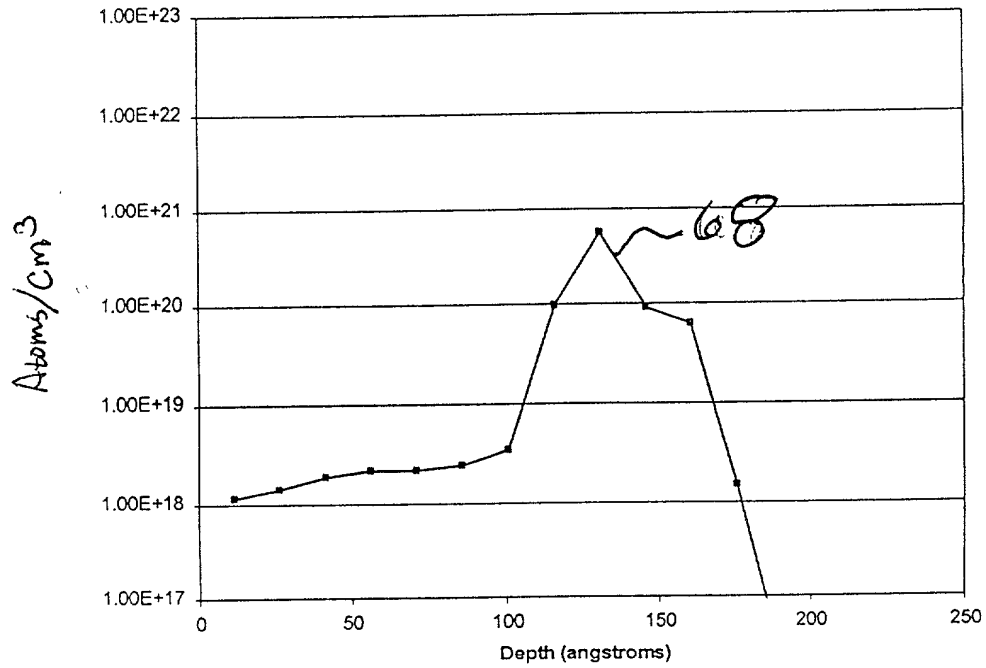

1.00E+23
1.00E+22
1.00E+21
1.00E+20
1.00E+19
1.00E+18
1.00E+17
Atoms/cm3
68
0
50
100
150
200
250
Depth (angstroms)

Fig. 15